Radiant heating of a Bio-oil droplet:
A quest for a suitable model and scaling of pre-explosion conditions

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Abstract

A suitable model for radiant heated single drop of bio-oil is discussed. The main efforts of the study are stressed on a discussion of models of droplet heating and scaling of the pre-explosion conditions.

Introduction

Bio-oil is a liquid fuel produced by the pyrolysis of biomass. In Australia, research on bio-oil production has been undertaken on the slow pyrolysis of a number of indigenous tree species (i.e., *Eucalyptus globulus* and *Eucalyptus camaldulensis*) that can be grown sustainably in plantations. The bio-oil produced is a dark, viscous liquid with smoky odour, it contains negligible sulphur, and it is relatively high in oxygenated compounds. Due to its plantation origins, it is a renewable resource and can be greenhouse gas neutral when used as a fuel. These attributes make bio-oil an alternative liquid fuel source for both power generation and transport. The composition and properties of bio-oil depend on the biomass source and pyrolysis rate used in its production. The elemental composition of bio-oil resembles that of biomass [1-3]. Bio-oil fuel-related characteristics are provided in [4-6].

The oxygen-rich nature of the principle components of wood (lignin, cellulose and hemicellulose [7]) affects the combustion behaviour of these pyrolysis derived liquids. The high oxygen content results in low-energy heating value that is less than 50% of that for conventional fuels. In general, these liquids are combustible, but no flammable (from safety point of view) due to the high content of non-volatile components that require high energy for ignition. Combustion tests on single bio-oil droplets derived from oak and pine [8-9] indicated: (a) A multistep process: ignition, quiescent burning emitting blue radiation, droplet micro-explosion, disruptive sooty burning of droplet fragments emitting bright yellow radiation, formation and burnout of cenosphere particles; (b) A very wide range of boiling temperatures, which is a result of the bio-oil chemical composition. The oils start boiling below 100°C, the distillation stops at 250-280°C, leaving 35-50% of the starting material as residue. Therefore, the bio-oils do not exhibit complete vaporisation before combustion, unlike the mineral hydrocarbons; (c) Droplets of less severely cracked pyrolysis oils exhibit shorter pre-explosion time and less effective micro-explosion. Oils that underwent severe cracking during the pyrolysis exhibit large pre-explosion times and more violent micro-explosions that results in more rapid burnout unlike the lighter oils. This behaviour depends on the oxygen content and pyrolysis process. Severe cracking reduce both the organic liquid yields and the oxygen content; (d) A strong relation between the moisture content and bio-oils combustion behaviour. The moisture content varies over a wide range (15-30%). It is a product of the original moisture in the feedstock and also the water produced from dehydration reactions occurring during pyrolysis. At this concentration, water is usually miscible with the oligomeric lignin-derived components, because of the solubilising effect of other polar hydrophilic compounds (low molecular weight acids, alcohols, hydroxyaldehydes and ketones) mostly originating from the decomposition of carbohydrates. Despite the high moisture content, the adiabatic flame temperature of the bio-oil is relatively high, 1700-2000 K compared to 2200-2300 K for standard fuels [10].

The present communication considers scaling of the pre-explosion conditions. The paper is developed as follows: (a) Analysis of existing models of explosive boiling of liquid droplet and their adequacy to behaviour of bio-oils; (b) Creating of physical and mathematical model for scaling and definition of dimensionless groups controlling the process; (c) Analysis of the pre-explosion conditions and an attempt to derive scaling estimates.

Models

Explosive boiling of liquid droplets

There are existing models of explosive boiling of droplets [11-13] that are verified by experiments [14-15]. The applicability of these models is discussed below.

Shusser and Weihs [13] proposed a model (see Figure 1a) based on the assumption of a constant evaporation rate equal to its maximal possible value. The kinetic theory [16] limits the maximal evaporation rate to the mass flux through the core (bubble)

$$J_V = p_s \sqrt{\frac{M}{2\pi R T_s y}} \qquad (1)$$

where J_V is the evaporation rate, T_s is the boiling temperature for the droplet liquid, p_s is the saturation pressure at this temperature, M is the molar mass of the vapour and R is the universal gas constant. Shusser and Weihs [13] analysed and simplified the model of Prosperetti [17] to yield equations for the gas density, $\rho_G = J_V / \dot{R}_1$, and pressure, $p_i = \rho_G (R/M) T_s$ inside the core. Here $\dot{R}_1$ is the core (bubble) growth rate

$$\dot{R}_1 = b_0 \left(\frac{2}{3} \frac{J_V}{\rho_1} \frac{R}{M} T_s \right)^{1/3} \qquad (2)$$

ρ_1 is the density of the host fluid, b_0 is an empirical constant that is 0.96 for butane, 0.97 for water, 0.94 for pentane. Shusser and Weihs [13] suggested that $b_0 = 1$ in equation 2, can be considered as a good approximation for the bubble growth rate.

Fu et al. [18] proposed a model of micro-explosions suitable for both oil-in-water (O/W) and water-in-oil (W/O) emulsified droplets. The authors suggested an empirical model (see Figure 1b) and a criterion for explosion expressed as

$$\frac{4}{3}\pi\left(R_0^3 - R_1^3\right)(1-\phi) = \frac{4}{3}\pi\left[\left(R_1 + d\right)^3 - R_1^3\right] \quad (3)$$

where R_0 is the initial radius of the emulsion droplet, R_1 is radius of the emulsion core and d is the diameter of the dispersed micro droplet, ϕ is the water volumetric percentage.
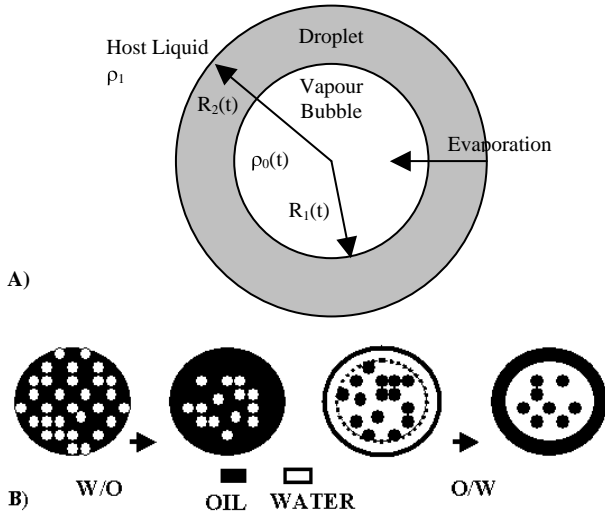

Fig. 1 Existing models of explosive boiling of bi-component droplets: a) Shusser and Weihs [13]; b) Fu et al. [18].

Fu et al. [18] suggested that a micro-explosion occurs when an oil membrane covers the water inside the micro droplets. Equation (3) implies that the volume of the membrane equals the volume of pure oil in the droplet.

Equivalent Models applicable to Bio-oils

Assumptions

The models commented above have been tested with pure liquids and hydrocarbons. These conditions differ significantly from those existing in bio-oil droplets. First of all, the bio-oil droplets are neither bi-component with gaseous cores, nor emulsion ones. Combustion experiments [8] show a shell formation that is relatively dry with respect to the remaining part of the droplet liquid. Looking at the pre-explosion process it can be assumed that the droplet diameter remains practically unchanged ($\dot{r}(t) = const$). This is a very strong simplification since Wornat et al. [8] reported droplet swelling by up factor of 3 in diameter prior to rupture. However for the preliminary scale analysis this fact and the hydrodynamic conditions might be ignored. The further analysis look for an equivalent model that simultaneously satisfies two major conditions: (i) to be geometrically identical to the bio oil droplets and (ii) to permit the use the ideas of the two models commented above. The basic geometric assumption of the equivalent model is that the entire water forms a core with expanding radius and growing pressure, while the rest of the bio-oil material forms a membrane (shell).

Accepting of this equivalent bi-spherical model we attain several advantages: (a) In a situation of scarce physical data and large variations of properties of bio oils the first attempt to solve the problem is to use macroscopic data relevant to the water content; (b) Both, the water content of the bio-oil and the drop size can be experimentally found; (c) In general, droplet burning (or evaporation) results in moving boundary problems. However, the assumption of a constant droplet size allows applying the classical heat transfer equation with fixed boundaries [19,22], and scaling methods [20] and results from the combustion of W/O emulsions [21].

Heating of a single droplet - basic equations and approximations

Assuming a spherically symmetrical temperature distribution inside the droplet of a radius R_d and an external radiation flux rate, $\dot{q}''$ [22], the transient heat conduction equation for the internal droplet volume is

$$c_o\rho_o\frac{\partial T}{\partial t} = k_o\left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r}\frac{\partial T}{\partial r}\right) + \dot{q}'''(r) \quad (4)$$

where $\dot{q}'''(r) = \partial\dot{q}''/\partial r$, r is the radial distance, c_o, ρ_o and k_o are the liquid specific heat capacity, density and thermal conductivity. It can be assumed that the Bouguer law is valid [20], i.e. $\dot{q}''(r) = \dot{q}''\exp(-\mu r)$, where μ (m^{-1}) is the effective average radiation absorption coefficient. If the droplet is heated by radiation only by the feedback from the surface flame and the convection is ignored the energy balance at the surface ($r = R_d$) is the Stefan boundary condition (SBC) [20, 23]

$$\dot{q}'' + \rho_o L\dot{r}(t) = k_o\frac{\partial T}{\partial r}\bigg|_{r=R_d} \quad (5)$$

where L is the specific heat of evaporation. The second boundary condition is $(\partial T/\partial r)|_{r=0} = 0$. The initial condition is $T = T_\infty$ at $t = 0$.

Scaling

The classical approach is to accept a dimensionless temperature $\Theta = (T - T_\infty)/(T_s - T_\infty)$ and the droplet radius as a length scale ($\tilde{r} = r/R_d$). Therefore, the dimensionless forms of equations (4) and (5) are

$$\frac{\partial\Theta}{\partial\tilde{t}} = Fo\left(\frac{\partial^2\Theta}{\partial\tilde{r}^2} + \frac{2}{\tilde{r}}\frac{\partial\Theta}{\partial\tilde{r}}\right) + \frac{\mu\dot{q}''(\tilde{r})\tau_0}{\rho_o c_o(T_s - T_\infty)}\exp\left[-(\mu R_d)\tilde{r}\right] \quad (6)$$

$$\underbrace{\frac{\dot{q}''R_d}{k_o(T_s - T_\infty)}}_{B_{SA}} = \underbrace{\frac{L}{c_o(T_s - T_\infty)}}_{Ste}\underbrace{\frac{R_d\dot{r}(t)}{a_o}}_{Pe} - \frac{\partial\Theta}{\partial\tilde{r}}\bigg|_{\tilde{r}=1} \quad (7)$$

where, B_{SA} is a dimensionless number analogues to the Biot number in case of forced convection (the subscript means *Surface Absorption*) [20], *Ste* and *Pe* are the Stefan and Peclet numbers. Equation (6) provides three dimensionless groups: Fourier number ($Fo = t/\tau_0$), where $\tau_0 = R_d^2/\alpha_o$ is the thermal diffusion time; Bouguer number ($Bu = \mu R_d$) and

$$N_{VA} = \frac{\mu\dot{q}''\tau_0}{\rho_o c_o(T_s - T_\infty)} = \underbrace{(\mu R_d)}_{Bu}[\underbrace{\frac{\dot{q}''R_d}{k_o(T_s - T_\infty)}}_{N_0}] \quad (8)$$

Here N_{VA} (the subscript means *Volumetric Absorption*) is a radiation-conduction number [22] analogous to the Stark number [23], that can be presented as a product $N_{VA} = BuN_0$ since $\dot{q}'''(r) = \partial\dot{q}''/\partial r$.

Dimensionless groups and functional relationships

The classical dimensionless solution provides a relationship

$$\Theta = \Phi(Bu; N_0, Ste, Pe) \qquad (9)$$

Considering the evaporation rate J_V (from equation 1) and fixing $T = T_s = T_L$, the kinetic superheat limit can be defined. At $T = T_L$, Θ becomes a constant $\Theta = \Theta_L$. If the time of the micro-explosion, t_e is known, then a pre-explosion Fourier number can be defined as $F_o^e = t_e/\tau_0$ that yields

$$F_o^e = \Psi(\Theta_L Bu, N_0, Ste, Pe) \qquad (10)$$

The function $\Psi = \Phi^{-1}$ depends on the type of the analytical solution.

Minimisation of the number of dimensionless groups

Minimisation of the number of dimensionless groups performed in [20] yields a new dimensionless number $H_p = \dfrac{B_{SA} Ste}{Pe} = \dfrac{\dot{q}''}{\rho_o \ddot{r} L}$. This allows F_o^e to expressed as $F_o^e \approx H_p^n Bu^m N_0^s$ [19], since the relationship between F_o^e and Bu and N_0 is defined in equation (7) while H_p from SBC defines the pre-factor of the power-law relationship. The exponents (n, m, s) can be defined through scaling of experimental data.

Alternative scales

The analysis provided in [20] yields that for radiation-conduction problems with SBC at the interface (liquid-flame) a more adequate length scale is $Z_0 = \dfrac{k_o(T_s - T_\infty)}{\dot{q}''}$, which automatically leads to SBC in a form $1 = \dfrac{1}{H_p} - \dfrac{\partial \Theta}{\partial \tilde{r}}$. The time scale is $\tau_a = (\mu a_o^2)^{-1}$ that defines $\tilde{F}_o^e = \mu a_o^2 t_e = Bu^2 F_o^e$.

Analysis
Approximate solutions

As reported in [24] the approximate solution of equations (4) and (5) is

$$T - T_\infty = \frac{\alpha \dot{q}'' R_d}{k_o}\left[1 - \exp\left(-3\frac{k_o t}{\rho_o c_o R_d^2}\right)\right] \qquad (11)$$

where α is a dimensionless coefficient (in terms of the present analysis $\alpha = Bu$). The dimensionless form of equation (11) is

$$\Theta = \frac{T - T_\infty}{T_s - T_\infty} = Bu N_0[1 - \exp(-3F_o)] \qquad (12)$$

When $T = T_L$ the RHS of (12) becomes the parameter Θ_L and the time t_L can be scaled as

$$F_o\big|_{T=T_L} \equiv \underbrace{H_p^m}_{BC} n \underbrace{\frac{1}{1 - \Theta_L/Bu N_0}}_{heat \ diffusion \ in \ the \ droplet} \qquad (13)$$

Asymptotic (extreme) situations

Two asymptotic situations relevant to the two term of RHS of equation (4) may be considered [22]: (a) Heat conduction dominating mechanism (HCD) with a surface absorption ($\dot{q}'''(r) = 0$) only; and (b) Heat absorption dominating mechanism (HAD) with a dominating source term.

Following the analysis of [20], the HCD requires a condition $N_{VA} << 1$ that leads to $Bu N_0 << 1$ or $N_0 << 1/Bu$. The HAD mechanism with dominating source term imposes the condition $\dfrac{Bu}{N_0}\dfrac{1}{\exp(-\mu S_L \tilde{r})} << 1$ where S_L is the process length scale. Here $\exp(-\mu S_L \tilde{r}) \le 1$, where 1 corresponds to the droplet surface. Taking into account that $1/\exp(-\mu S_L \tilde{r}) > 1$, a more weak, but sufficient condition is $Bu/N_0 << 1$ or $N_0 >> Bu$. These inequalities permit to estimate the magnitude of N_0 if the values of Bu are known. The HAD mechanism yields $\Theta = \left(\dfrac{N_0}{Bu}\right)^2\left[\tilde{F}_o^2 - \dfrac{Pe}{N_0}\tilde{F}_o\right]$. The result can be simplified as $\tilde{F}_o \approx \sqrt{\Theta}\dfrac{Bu}{N_0}$ since $Pe/N_0 << 1$ (the hard shell implies low values of Pe). Furthermore, since $\tilde{F}_o^e = Bu^2 F_o^e$, F_o^e becomes $F_o^e \approx \sqrt{\Theta}\dfrac{1}{Bu}\dfrac{1}{N_0} \propto \dfrac{1}{Bu}$. Therefore, this scale analysis yields that

$$F_o^e \propto \frac{1}{Bu}H_p \qquad (14)$$

The condition $N_0 >> Bu$. applied to (13) through the weak condition $1/Bu N_0 << 1/Bu$, which leads to

$$F_o^e \propto \frac{\Theta_L}{Bu}H_p \qquad (15)$$

The further analysis will use the relationship given in equation (1). Generally equation (1) provides that $T_L \approx (1/J_V)^2$ (T_s is replaced by T_L to avoid ambiguities, since at $T = T_s$, Θ becomes unity). Thus, $\Theta \approx \propto (1/J_V)^2$ (following the definition of Θ) that yields (via equation 15)

$$F_o^e \propto (1/J_V)^2 \frac{1}{Bu}H_p \qquad (16)$$

In an explicit form equation (16) leads to $t_e \propto (1/J_V)^2$. Physically equation (16) implies that high evaporation rates lead to shorter pre-explosion times and *vice versa*. The other components of equation (16), Bu and H_p affect the pre-explosion time through: (a) High values of Bu implies high droplet absorptivity, a dominating HAD mechanism, higher evaporation rates and as a result shorter pre-explosion times. Low values of Bu, implies a dominating HCD mechanism and larger pre-explosion times; (b) The H_p number controls the radiation-conduction heat transfer through the droplet surface. Generally, the HAD mechanism is physically relevant to high water contents of the droplets, where occurrence of volume heat sources and nucleation evaporation can be expected. If the water content is not high, the head conduction is the dominating mechanism, which does not lead to intensive vapour nucleation. This comment is consistent with the experiments analysed in [21] where the evaporation rate increases linearly with the increase of the water content (emulsion volume).

Remarks on the scaling estimates

As commented in [21] the increase of the water content (emulsion volume) leads to higher evaporation rates and shorter

pre-explosion times. It is likely that the micro-explosions would be ruled primary by the explosive evaporation of water for low volatile fuels. Water is only superheated inside less volatile hydrocarbons-based emulsions. Bio-oils behave similarly because of the high amount of low volatile and non-volatile components [9]. The estimate given in equation (16) is consistent with these facts [21]. The analysis in [8], show that oak oil droplets with 16.1 wt% water content explode after 34.8 ms, while droplet of diesel fuel #2 (a negligible water content) has a pre-explosion time of 149 ms.

The scaling estimate derived here is based on the analysis of heat transfer equations, which allows to define the controlling parameters. If a dimensionless nucleation rate is defined as $N_J = J/J_V$, where J is a nucleation rate at temperature $T < T_s$ for water, equation (16) can be expressed as

$$F_o^e \equiv \left(\frac{1}{N_J} \frac{1}{J_V} \right)^2 \frac{1}{Bu} H_p \qquad (17)$$

The main idea of equation (17) is that via analysis of experiments the value of N_J can be determined. Such analysis would estimate the apparent values of J for bio oils, since J_V is known for water and pure liquids [23] only. The latter would allow evaluating the applicability of the homogeneous nucleation theory to bio oils.

Special mathematical symbols:

$\propto$ - *proportional to*;

O - *order of magnitude*;

$\approx$ - *about equal*;

$\equiv$ - *identical (equivalent to)*;

$a \sim b$ - **a** *scale to* **b** *as well as*;

$\Rightarrow$ - *it follows that (implies)*;

$a \rightarrow b$ - **a** *approaches* **b**;

$|\ |$ - *absolute value*.

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